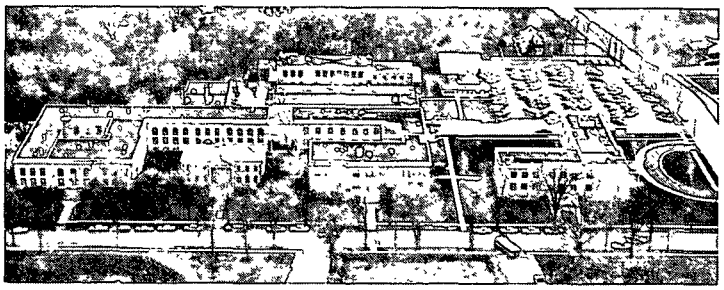

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 228

THE REACTION OF PINE KRAFT PULPS WITH POTASSIUM SUPEROXIDE

N. S. THOMPSON AND H. M. CORBETT

MARCH, 1987

The Reaction of Pine Kraft Pulps with Potassium Superoxide

N. S. Thompson and H. M. Corbett

This manuscript is based on results obtained in IPC Project 3474 and is to be presented at the TAPPI Oxygen Bleaching Conference in San Diego, CA on June 7-12, 1987

THE REACTION OF PINE KRAFT PULPS WITH POTASSIUM SUPEROXIDE

N. S. Thompson
Emeritus Professor
The Institute of Paper Chemistry
Appleton, WI 54912

H. M. Corbett
Chemical Sciences Division
The Institute of Paper Chemistry
Appleton, WI 54912

ABSTRACT

An examination of the reaction of unbleached pine kraft pulps with potassium superoxide in DMSO has provided a model of what might happen to pulp during oxygen bleaching. The pattern of degradation follows closely that of the reaction of cotton fibers and suggests two types of behavior. One is surface erosion and the other involves degradation of the amorphous regions of cellulose. The dependence of the extent of tracheid degradation on an optimum quantity of lignin demonstrates the importance of fiber architecture and composition to degradation. The significance of these observations to oxygen bleaching is discussed.

INTRODUCTION

Previous research has shown that tracheids suspended in dimethyl sulfoxide (DMSO) react with potassium superoxide (1). This unexpected result (2,3,4) was first throught to arise from the participation of lignin radicals. Since cotton fibers were later found to react similarly, lignin by-products need not be an intermediary. Thus many organic radicals and complex reaction pathways must participate (5). The present investigation was undertaken to explore the effect of DMSO, lignin and fiber structure on the manner in which superoxide degrades tracheids.

EXPERIMENTAL

The apparatus used in these experiments is that described in previous publications (1,5). The pulps employed were several laboratory pine kraft pulps (kappa 19, 35, 95, 150), spruce kraft pulp (kappa 16), and holocelluloses prepared from pine, spruce, and cedar by a mild chloriting technique (6). The reactors consisted of Teflon-sealed glass vessels in which 1 g pulp suspended in 75 mL DMSO was shaken at room temperature on a Kahn shaker (1.5 inch stroke and predetermined rates) with 150 mg powdered KO_2.

Tests were conducted comparing the effect of DMSO and pyridine as media for the reaction (7). Similar chemical and physical degradations were observed although the reactions in pyridine required 12 to 16 hours for completion. This reflects the lower solubility of KO_2 in pyridine compared to DMSO (1 mM vs. 7 mM). The highly polar DMSO penetrates pulp better than pyridine but does not break hydrogen bonds (8). Other control experiments showed that Na_2O_2 did not react with pulp suspended in DMSO.

Reactions were stopped at suitable intervals and the pulps were reacted with 20 mL aqueous methanol (1:10) to destroy excess superoxide. The residue was washed with sufficient water to remove remaining DMSO and undissolved KOH. This alkaline solution extracted oxidized organic material. Samples for chemical analysis were air dried while the samples for SEM analysis were isolated by critical point drying from CO_2. The static reactor used here was described previously (5).

Conventional SEM techniques were used in preparing samples for examination with a JOEL JSM 35C scanning microscope. Other tests employed were kappa determinations (9), viscosity tests (10), molecular weight determinations using HPLC techniques (11), fiber length measurements (12), FT-IR spectra (13), and sugar analysis (14).

RESULTS

The effect of lignin content on the reaction of pine kraft pulps with superoxide is shown in Fig. 1. The existence of an optimum lignin content indicates greater lignin contents offer protection by minimizing yield loss and carbohydrate degradation. Very low levels of lignin also inhibit yield loss by the reaction.

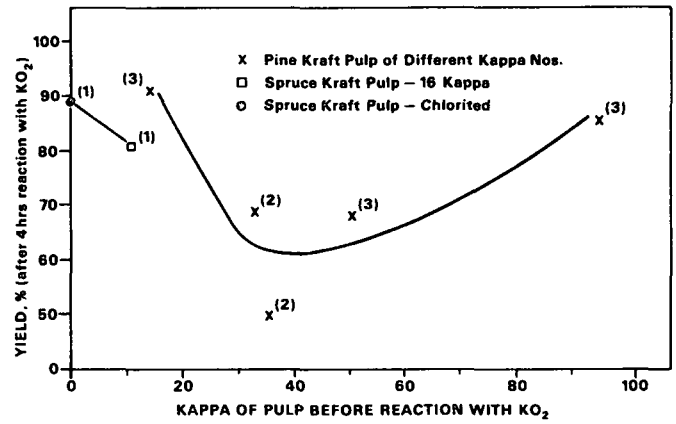

Fig. 1 The relationship between pulp yield (after 4 hours with superoxide) and initial kappa number.

The loss of yield and chemical constituents with time of reaction by these treatments is consistent with this behavior and is shown in Fig. 2 and 3. Both hemicellulose and lignin are rapidly removed and cellulose degradation and removal occurs more slowly. These behaviors are probably due to changes in accessibility as a result of lignin encapsulation and cellulose hornification and to the high DP of cellulose itself.

Samples which had been exhaustively extracted with aqueous methanol to remove all KOH before isolation did not exhibit significant structural alterations when viewed by SEM. When water is used to remove the resulting alkali and DMSO, oxidized organic material (confirmed by FT-IR) is removed as shown above. The progress of erosion can then be followed by SEM and shows progressive visual damage with time of reaction.

The SEM pictures indicate the erosion of tracheids by KO_2 proceeds between wall layers (Fig. 4) as well as between fibrils (Fig. 5, not extracted) and (Fig. 6, extracted).

1

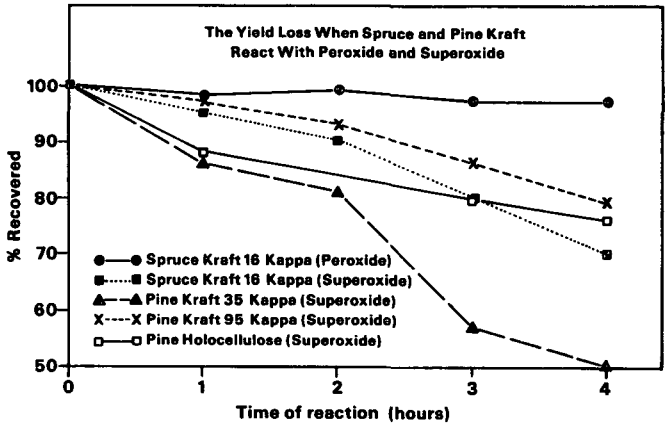

Fig. 2 The loss of yield when spruce and pine kraft pulps react with peroxide and superoxide.

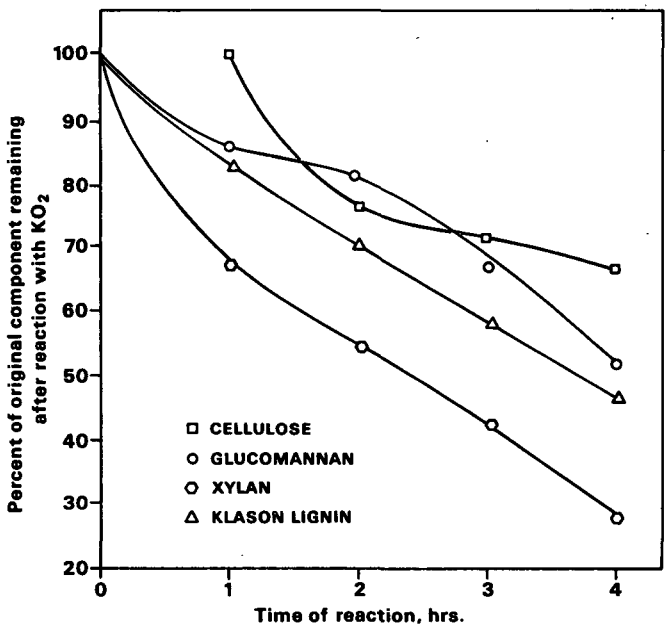

Fig. 3 The loss of yield of components from southern pine kraft pulp (95 kappa) reacted with superoxide in DMSO.

Attempts to change the effect of mechanical action on variety of fibrous substances are shown in Fig. 7. Less violent shaking during the reaction does indicate a slight decrease in fiber damage. Note that viscose fibers are also broken. A better indication of the effect of stress is seen in Table 1 in which a comparison is made between the effects of reactions in a static reactor and in the shaking reactor. The degradation of cellulose by superoxide at the optimum lignin level (35 kappa) for carbohydrate degradation and fiber length reduction under the two conditions is shown in Table 1. HPLC analysis of degraded kraft pulps [like the behavior of cotton (5)], proceeds to a limiting value similar to the leveling off DP for acid hydrolysis.

Fig. 4 Southern pine holocellulose reacted 4 hours with KO_2, 3000X.

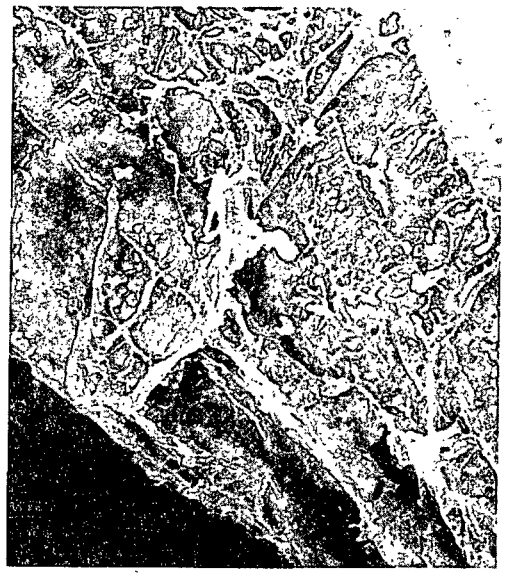

Fig. 5 Southern pine holocellulose reacted 3 hours with KO_2, 6000X.

Table 1 The effect of passing KO_2 in DMSO through a pad of southern pine kraft pulp (35 kappa)

Reaction	Viscosity, cp	Kappa	Fiber Length
Unreacted[a]	26.1	30	1.3 mm
Reacted 4 hours (static)	6.1	n.a.	~1.2 mm
Reacted 4 hours (shaken)	2.9[b]	n.a.	0.6 mm

[a]Peroxide bleaching diminishes the viscosity to 21.7 cp.
[b]Cotton of similar viscosity had DP = 300.

2

Fig. 6 Southern pine holocellulose reacted 3 hours with KO_2, 6000X.

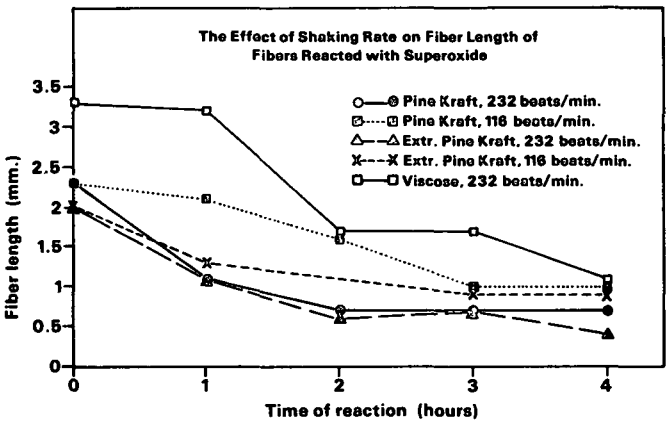

Fig. 7 The effect of shaking rate on fiber length of fibers reacted with superoxide.

The behavior of tracheids parallels the behavior of cotton under these conditions (5). Molecular weight determinations by HPLC of carbanilate derivatives was not done, but it is assumed that the DP distribution, like that of cotton, is symmetrical, suggesting random cleavage of cellulose chains. The limiting viscosity (Fig. 8) shows that cellulose microfibrils have been cleaved by superoxide. This is apparent in the case of broken tracheids, and in broken fibrils in the cell walls (Fig. 4). The degradation manifests itself to its greatest extent when a mixture of oxidation mixture of fibers and broken fibers is beaten ultrasonically in water. Instead of the anticipated fibrillation, the particles were broken into small pieces (Fig. 9).

DISCUSSION

The results confirm the observation that superoxide does degrade the chemical constituents and structure of tracheids in contrast to its relative inertness toward lignin (2) and carbohydrate (15) models in solution. In addition, degradation increases with diminishing lignin content of pulps to a maximum value. This behavior results from changes in lignin encapsulation and cellulose hornification. Holocelluloses devoid of lignin react with greater facility than lignin free pulps, presumably because of greater accessibility and the less crystalline nature of hemicellulose.

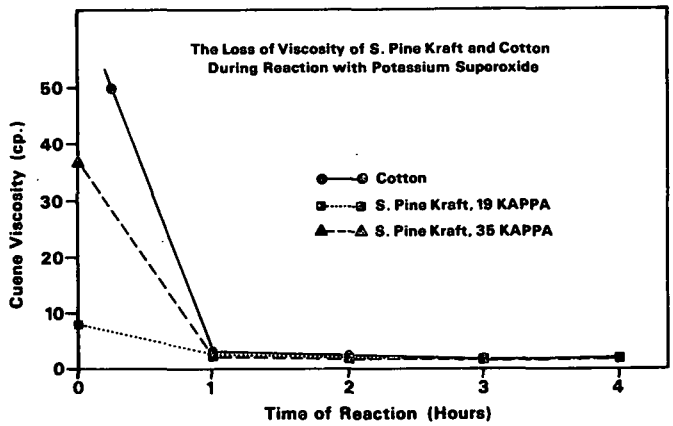

Fig. 8 The loss of viscosity of tracheids during reaction with KO_2.

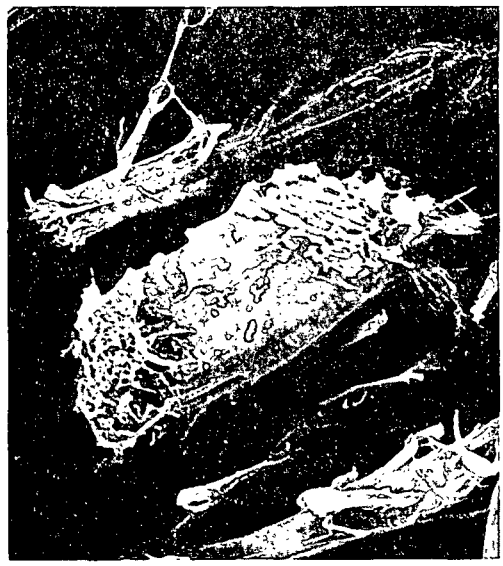

Fig. 9 Southern pine holocellulose reacted 4 hours with KO_2, 7000X.

The data suggest that degradation proceeds first along easily accessible features such as surfaces of fibers, between fiber walls and even between fibrils and not into crystalline regions. (Avicell is not greatly affected.) The most unusual feature is the rapidity with which a limit DP is achieved. In the case of cotton, the degradation achieved in 4 hours would require 1 year with HCl under similar constraints (5). Thus the degradation must penetrate the amorphous regions of cellulosic microfibrils. The weakened fibers are easily shattered by mechanical treatments.

The reactions responsible for this degradation

3

are complicated by the anamolous chemical behavior of KO_2. Intermediates derived from its reaction with organic substances are claimed to be responsible (4) (Reactions 1 and 2). The organic radicals derived from both lignin and carbohydrates are active participants here, but how they are formed in the first place is not known. It is unlikely that radicals derived from DMSO are the only participants, since degradation also proceeds in pyridine [although at a slower rate (6)]. In reactions (1) and (2) R is derived from lignin, polysaccharide and solvent.

$$KO_2 + R{:}H \longrightarrow K^+ + {}^-O_2H + R\cdot \qquad (1)$$

$$\longrightarrow =O_2 + {}^1O_2 + ROO^- + ROO\cdot + \cdot OH + \cdot O_2 + O_2 + R\cdot \qquad (2)$$

Whatever its origin, the erosion that occurs is of 2 types. One proceeds through the accessible regions of the wall that are rich in lignin and hemicellulose. Lignin and carbohydrates do form radicals of varying degrees of stability and these could be formed from the undefined reactions with KO_2. Penetration of this region occurs by slipping between and/or breaking hydrogen bonds before attacking the fiber. Some organic fragments would be too large, but the smaller ones might do so until stopped by extensive hydrogen bonding. Since lignin-rich pulps are not degraded as rapidly as holocelluloses, hemicelluloses and other amorphous polysaccharides must provide a better pathway for the reaction to follow than lignin.

The other type involves the rapid loss of cellulose DP and implies penetration of cellulosic microfibrils. Since a limit DP cellulose is obtained similar to that from acid hydrolysis, this degradation must also have proceeded through the amorphous regions of the microfibril. Penetration of this region by reactants is made difficult by the small size of intermolecular distances and the relative rigidity imposed by the associated crystalline matrix. Small molecules such as H^+, ^-OH and H_2O, do penetrate and it is likely that $-O_2H$, $\cdot O_2H$, O_2, $\cdot OH$ and $^1O_2$ also do so. The rapidity of this degradation compared to acid hydrolysis suggests that a radical chain mechanism is involved. The degradation would be assisted because of the relatively high concentration of carbohydrate in these noncrystalline regions relative to that of quenching agents. These molecules form radicals which react rapidly to form peroxyl radicals as described by von Sonntag et al. (3,16). These could react with adjacent polysaccharides to form peroxides and thus propagate the reaction. The reaction can occur only if competing reactions to eliminate superoxide from peroxy radicals are minimized.

$$\begin{array}{c} | \\ -C-OH \\ | \\ H \end{array} + \begin{array}{c} | \\ -C-OH \\ | \\ \cdot \end{array} + O_2 + \begin{array}{c} | \\ -C-OH \\ | \\ O-O\cdot \end{array} + R{:}H + \begin{array}{c} | \\ -C-OH \\ | \\ OOH \end{array} + R\cdot \qquad (3)$$

Amorphous regions do not penetrate all the way across degraded tracheids, since they are not broken unless stressed. Celluloses themselves must differ, since other experiments show the cellulose of Acetobacter xylinum (unlike vegetable cellulose) is not "tenderized" by the action of superoxide (17).

Because of the idealized reaction conditions, the observations made here cannot be directly applied to predict the behavior of pulps during commercial bleaching. They do demonstrate that radicals can attack cellulose and that the mechanisms involved are exceedingly complex and might involve chain reactions of a novel type. The results also suggest that the behavior of heterogeneous systems differs greatly from reactions in solution. It remains to be proven whether similar reactions occur in aqueous bleaching systems. If so, they are probably much more limited in scope.

CONCLUSIONS

Superoxide reacts with lignin and carbohydrate in pulp. In contrast, it does not react to the same extent with model systems in solution. Degradation is maximized at a critical lignin concentration. A chain reaction is speculated to occur, since the degradation proceeds very rapidly through accessible amorphous regions of fibers. The nature of the initiating species is not known, but once initiated, the reaction is probably propagated by those radicals derived from carbohydrates and oxygen shown to exist in the literature.

REFERENCES

1. Thompson, N. S. and Corbett, H. M., Tappi 64 (5):126(1981).
2. Barkau, R., Bastian, J., and Thompson, N. S., Tappi 68(10):110(1985).
3. Schuchmann, M. N. and von Sonntag, C., Z. Naturforsch. 33B:329(1978); J.C.S., Perkin Transaction's II, 1958(1977).
4. Singh, A., Can. J. Physiol. Pharm. 60(11):1330 (1982).
5. Thompson, N. S. and Corbett, H. M., Tappi 68 (12):68(1985).
6. Thompson, N. S. and Kaustinen, O. A., Tappi 47(3):157(1964).
7. Thompson, N. S., Unpublished research, The Institute of Paper Chemistry, 1984.
8. Parker, A. J., Quarterly Rev. 163, 1962.
9. TAPPI T 222 os-74.
10. TAPPI Test Method T 230.
11. Schroeder, L. R. and Haigh, F. C., Tappi 62 (10):103(1979).
12. Pfaffli, M. S. I. and Alfthan, G., Paperi Puu 39:509(1957).
13. McKelvey, R. D., Thompson, N. S., and Lyse, T. E., Cell. Chem. Tech. 17:355(1983).
14. Borchardt, L. and Piper, C., Tappi 53:257 (1970).
15. Molinarolo, S. and Thompson, N. S., Unpublished research, The Institute of Paper Chemistry,

4

1984.

16. Bothe, E., Schuchmann, M. N., Schulte-Frohlende, D., and von Sonntag, C., Photochem. & Photobiol. 28(4/5):639(1978).

17. Thompson, N. S., Carlson, J., Kaustinen, H. M., and Uhlin, I., submitted for publication, 1987.

5